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by

Tadahiro Sunaga, Kenneth J. Ivin,[†] Gretchen E. Hofmeister, John H. Oskam,
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Abstract

Ring-opened polymers of (+)- and (±)-*endo,exo*-5,6-dimethylbicyclo[2.2.1]hept-2-ene (**1**) having cis double bond contents between 5 and 85% were prepared using $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})(\text{OR})_2$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$; $\text{OR} = \text{OCMe}_3, \text{OCMe}_2(\text{CF}_3), \text{OCMe}(\text{CF}_3)_2$) complexes as initiators. The cis content of the polymers increased in proportion to the electron-withdrawing power of the alkoxide ligands. ^{13}C NMR spectra (125 MHz) of these polymers were interpreted in terms of the various possible types of dyad structure: XX, XN (NX), NN, where X and N refer to substituents derived from *exo* and *endo* methyl groups, *m* and *r* refer to the meso (isotactic) or racemic (syndiotactic) configuration of adjacent cyclopentane rings in the chain, and *tt*, *tc*, (*ct*), and *cc* refer to the cis/trans double bond sequences. High cis polymer made from 98% (+)-**1** contained 78% *m* dyads and had more than twice the optical rotatory power and a higher T_g (85°C) compared to a high trans polymer (48% *m* dyads; $T_g = 55^\circ\text{C}$).

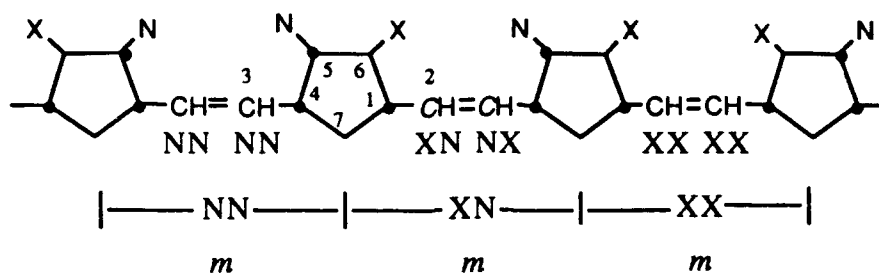
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INTRODUCTION

Molybdenum alkylidene complexes of the type $\text{Mo}(\text{CHR}')(\text{NAr})(\text{OR})_2$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$; $\text{OR} =$ various alkoxides and phenoxides; $\text{R}' = \text{CMe}_3$ or CMe_2Ph) (2) are useful initiators for the living ring-opening metathesis polymerization of cyclic olefins.¹⁻⁶ Recently it has been shown that syn and anti rotamers can have dramatically different reactivities and that the rate at which they interconvert correlates with the cis/trans (*c/t*) content in polymers of 2,3-bis-(trifluoromethyl)norbornadiene and 2,3-dicarbomethoxynorbornadiene.⁷

The microstructure of polynorbornenes and norbornadienes may be determined readily by ^{13}C NMR studies.⁸ The polymers that have been studied include various methyl-substituted norborn-2-enes (*exo*-5-methyl,⁹ *endo*-5-methyl,¹⁰ *syn* and *anti*-7-methyl,^{5,11} 1-methyl,^{12,13} 5,5-dimethyl,^{14,15} *endo,endo*-5,6-dimethyl,¹⁶ *exo,exo*-5,6-dimethyl,¹⁶ and *endo,exo*-5,6-dimethyl¹⁶) as well as norbornene itself.^{17,18} Polymers have been obtained that have a range of cis double bond contents ($\sigma_c = 0 - 1$) employing various classical metathesis catalysts as initiators. In all cases, one can observe *cc*, *ct*, (*tc*) and *tt* pairs in the ^{13}C NMR spectra of polymers that contain appreciable proportions of both cis and trans double bonds. For polymers made from unsymmetrical monomers fine structure also arises from the presence of head-head (HH), head-tail (HT), and tail-tail (TT) structures. A third type of fine structure, which is observed only for some carbon nuclei in certain polymers, arises from the fact that neighboring cyclopentane rings in the polymer chain may have either an isotactic (*m*) or syndiotactic (*r*) relationship. Tacticity has been determined by ^{13}C NMR methods for polymers made from unsymmetrical monomers.^{9,12-15} In these studies when partially resolved enantiomeric monomer mixtures are employed, the *m/r* ratio can be determined directly from the HT/HH ratio.

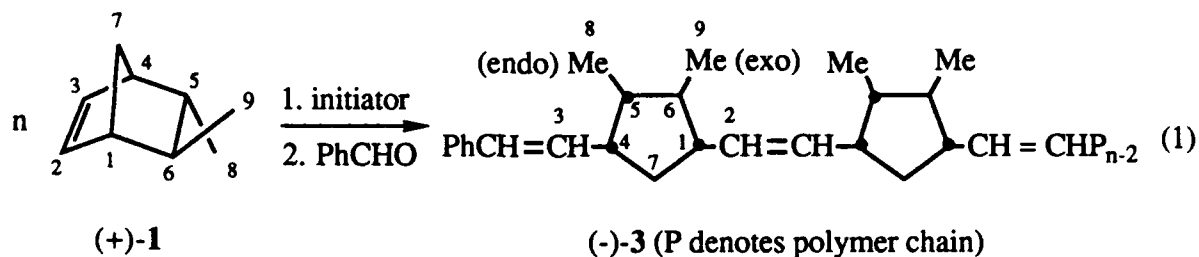
Poly(*endo,exo*-5,6-dimethylnorbornene) has been prepared previously, but only from (\pm)-1, using conventional initiators such as RuCl_3 , IrCl_3 and $\text{WCl}_6/\text{Bu}_4\text{Sn}$; the resulting polymers had a rather limited range of σ_c (0 - 0.3).¹⁶ Such polymers exhibit a form of HH, HT, TT isomerism that is more conveniently defined in terms of the relative positions of the substituents derived from the *endo*-methyl (N) and *exo*-methyl (X) substituents in the monomer. Thus one

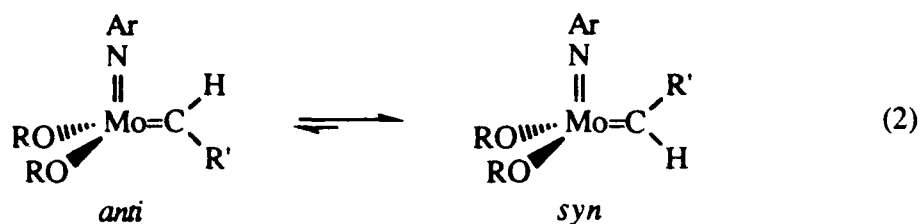


3 (derived from (\pm) -1; NX notation)

may distinguish between NN, XN and XX dyads. The carbons on the X side of an XN dyad are designated as XN and have different chemical shifts from those on the N side, which are designated as NX. As drawn, all the tactic dyads are *m* due to the opposite configuration of the allylic carbons on either side of the double bond. The double bonds may be *c* or *t*; note that adjacent cyclopentane rings will point in opposite directions in the trans isomer if the stereochemical relationship of the two allylic carbons is meso. The two central monomer units in 3 are derived from one enantiomer, the outer two from the other enantiomer. The ^{13}C NMR spectra of the high trans polymers showed evidence of *m/r* splittings, but the *m* and *r* assignments had to be made by analogy with related polymers.¹⁶

In the present work we report the preparation and polymerization of (+)-1 (equation 1) as well as (\pm) -1, initiated by 2a, 2b, or 2c (equation 2) to give polymers that have a much wider range of cis content ($\sigma_c = 0.05$ -0.85) than heretofore obtained. Compounds 2a, 2b, and 2c are known to be mixtures of anti and syn rotamers, with the syn rotamer being highly favored⁷).





2 a, OR = OCM₃; **2 b**, OR = OCM₂(CF₃); **2 c**, OR = OCM(CF₃)₂

¹³C NMR spectra also were obtained at a higher frequency (125 MHz) than in previous studies (62.8 MHz),¹⁶ and DEPT and HETCOR pulse sequences were also employed in order to assist in assignments. Therefore, a more accurate and detailed interpretation of the ¹³C NMR spectra has become possible.

RESULTS

Three polymers were prepared in >90% yields from (+)-**1** and three from (±)-**1**. The cis content was determined from ¹³C NMR spectra as described elsewhere;¹⁶ the results are listed in Table I. The polydispersities of the polymers are all low ($M_w/M_n < 1.2$), except for (-)-**3**, which suggests that these polymerization reactions are living and that the observed polymer structure is that produced in the primary polymerization reaction. M_n values determined by comparison with polystyrene standards were not consistent with the molecular weights calculated on the basis of the number of equivalents of monomer employed, but measurement of molecular weight by on-line viscometry gave molecular weight values close to those calculated, except for (-)-**3c**; the latter result suggests that a conformation other than a random coil is adopted by (-)-**3c**. T_g values increase with increasing cis content of the polymer, although not dramatically. Optical rotations of (-)-**3a**, (-)-**3b**, and (-)-**3c** are negative, while the optical rotation of the monomer is positive (Table I), and increase in magnitude as σ_c increases. However, CD spectroscopy showed only a transition analogous to that found for the monomer. Apparently if an ordered structure is adopted in solution, that structural form either is not inherently chiral, or if it is inherently chiral (e.g., a helix), one chirality is not favored over the other to a significant degree, even when the

resonance in Fig. 1b as a combination of XXm and XNr , while the outer resonances must be due to XXr and XNm . Likewise the central C_3 resonance, which is common to both Figures 1a and 1b, must be assigned to a combination of NXm and NNr , while the outer resonances must be due to NXr and NNm . To decide which of the outer resonances is which in Fig. 1b we may compare the predicted line positions (which take no account of m/r splitting) with the average positions of the four pairs of peaks. This results in the assignment of the trans peaks listed in Table II. The predicted line positions are slightly displaced from the observed average m/r positions but the relative positions agree within 0.1 ppm. The r/m splittings for all four dyads are in the same direction and of similar magnitude ($\delta_r - \delta_m = 0.18 \pm 0.05$ ppm). The intensities in Fig. 1a indicate that the trans dyads are atactic ($(\sigma_m)_t = 0.48$), while those in Fig. 1b indicate that the structure is unbiased with respect to XN : $(XN + NX)/(XX + NN) \sim 1$.

The main peaks in Fig. 1a arise from trans olefinic carbons in which the next nearest double bond is also trans (tt). However the sample contains 5% cis double bonds and the small pairs of peaks upfield from the two main pairs between 134-133 ppm are ascribed to the corresponding structures for tc pairs. The inequality of the two components of these small signals in the spectrum of 3a suggests that, as in 3c (see below), the cis dyads are predominantly isotactic (m). The shoulder and small peak slightly upfield from the main C_3 peak in Fig. 1a are also probably accountable in terms of tc counterparts of the two overlapping tt peaks (NXm and NNr). All tc peaks should have matching ct signals. Two of these are in the positions indicated; the other must be hidden.

The spectrum of 3c (Fig. 1f) consists of essentially four equal resonances for the cis dyads. The predicted line positions of the outer lines (XX , NN) are in good agreement with those observed, while the inner lines are somewhat farther apart than predicted (Table II). However, the overall agreement can be considered satisfactory, with the line order the same as for the trans resonances: XX , XN , NX , NN . There is no obvious m/r splitting, but it is readily apparent from the spectrum of (-)-3c (Fig. 1e), that $XN = NX > XX = NN$, i.e. that $(\sigma_m)_c > (\sigma_r)_c$. It is estimated that $(\sigma_m)_c = 0.78$ for this polymer.

The spectra of the polymers of intermediate cis content, (-)-**3b** and **3b** (Figs. 1c,d), are more complex because of *cc/ct* and *tt/tc* splittings. The correlation of line positions and assignments for the three polymers of (+)-**1** are given in Table III. In Table IV are listed the additional lines seen in the spectra of high trans (**3a**, Fig. 1b) and high cis (**3c**, Fig. 1f) polymers of (\pm)-**1**.

The line order for *r,m* deduced here is the same as that derived on a different basis in previous work,¹⁶ but the line order XX, XN, NX, NN is different from that previously deduced (XN, XX, NN, NX) on the assumption that the Ru-TFA-initiated polymer was fully XN-biased. (Ru-TFA is a complex of approximate formula $\text{Ru}_2(\text{CF}_3\text{CO}_2)_4 \cdot 3\text{H}_2\text{O}$).¹¹ The interpretation of the four-line spectrum of the olefinic carbons in the Ru-TFA-initiated polymer cannot yet be made because the relative line positions do not match exactly those reported here. On the basis of how the lines match up one of four outcomes is possible: (i) atactic, alternating XX-NN; (ii) syndiotactic, unbiased; (ii) isotactic, unbiased; (iv) atactic, fully XN-biased. Further experimental work will be required in order to settle this issue.

¹³C NMR spectra upfield of the olefinic carbon region for the six polymers are shown in Fig. 2a-f. Consider first the spectra of the high trans polymers (-)-**3a** and **3a** (Figs 2a and 2b). The spectrum of **3a** is a much better resolved version of that previously published (prepared employing RuCl_3).¹⁶ Note in particular the considerable fine structure observed for the closely separated C₄ and C₅ resonances; only a single unresolved resonance was observed in the 62.9 MHz spectrum. Line positions and assignments are listed in Table V. The overall assignments of resonances to C₁, C₆, C₄ and C₅, and C₇ were made by comparing observed and predicted shifts, as was done in the case of C₂ and C₃ (see above). Agreement is only within 1.5 ppm, which reflects the fact that the cumulative effect of *endo*-5-methyl and *exo*-6-methyl substitutions is not additive. The assignment for C₇ was confirmed by a DEPT experiment and the assignments for C₄ and C₅ were determined by means of a HETCOR 2D (¹³C-¹H) experiment.

The fine structure in Fig. 2a shows that the shifts for C₆, C₅, and C₈ are sensitive to *m,r*

dyads, while those for C₁, C₄, C₇ and C₉ are sensitive to *mm*, *mr*, *rm*, *rr* triads, correlated with X,N structure in each case. It is clear from the relative intensities that the trans centered dyads are nearly atactic, as already concluded from the intensities for the olefinic carbons. Thus it is difficult to make absolute assignments; those shown in Table V are made from the relative intensities on the assumption that σ_m is slightly less than 0.5. Confirmation of these assignments would require the preparation of a more tactic high trans polymer.

In 3a (Fig. 2b), there are four possible dyad structures, as listed for C₆ in Table V, and sixteen possible triad structures. Hence the spectrum is more complex and difficult to interpret because of the overlap of numerous lines. Thus the 16 possible environments for C₇ give rise to three lines in the approximate ratio 2:6:8, while for C₁ and C₉ there is a somewhat different distribution. A curious feature of the spectrum in Fig. 2a is the gap around 44.8 ppm. The intense resonance in this position in Fig. 2b evidently stems mainly from C₅ NN*m* and NX*r*, but may also contain a contribution from C₄ triads.

Let us now consider spectra of the high cis polymers, (-)-3c and 3c (Figs 2e and f). The line positions and assignments for the non-olefinic carbons are listed in Table VI. Small peaks due to the presence of 15% trans double bonds are marked on the spectrum in Fig. 2e. A DEPT spectrum showed that the *c*-C₄ resonance overlapped with a small *t*-C₇ resonance. *c*-C₁ and *c*-C₅ are predicted to have very similar shifts, but in fact they are separated by about 1.1 ppm. *c*-C₁ was identified as the downfield resonance from its position relative to *t*-C₁: $\delta_t - \delta_c = 5.1$ ppm, consistent with the range of values normally found for α -carbons in cis and trans isomers. Likewise $\delta_t - \delta_c = 5.7$ ppm for C₄. These assignments were confirmed by a HETCOR 2D (¹³C - ¹H) experiment.

The pattern of fine structure for the high cis polymers is rather different from that of the trans polymers. On the one hand there is a marked bias towards isotactic dyads (see C₂ and C₃ spectra), making assignment of the fine structure in Fig. 2e relatively easy. On the other hand, there is practically no *m/r* splitting of the individual XN, XX, NN or NX signals in Fig. 2f, except perhaps for C₄ NN (Table VI). C₆ and C₉ show no XX/XN splitting, nor does C₈ show

an NN/NX splitting. However, C_1 is split (XX/XN), as are C_4 and C_5 (NN/NX), and C_7 shows triad sensitivity. The values of $(\sigma_m)_c$ derived from the C_1 and C_5 fine structure in Fig. 2e were 0.77 and 0.78, respectively, in good agreement with that derived from C_2 and C_3 (0.78). The fine structure for C_1 , C_5 , C_7 and C_4 in Fig. 2f indicates at most only a slight NX bias in the high cis polymer made from (\pm)-monomer (NX/NN = XN/XX \sim 1.2). The approximately 1:2:1 intensity ratio for the C_7 peaks in Fig. 2f indicates that the center peak in Fig. 2e corresponds to two of the four triad structures listed in Table VI, but the detailed assignment is uncertain.

The spectra of the polymers of intermediate cis content, (-)-**3b** and **3b** (Figs 2c and d), indicate that the tacticities with respect to cis and trans double bonds are similar to those for the high cis and high trans polymers, respectively, i.e. $(\sigma_m)_c \sim 0.8$ and $(\sigma_m)_t \sim 0.5$. Therefore, to a first approximation the tacticities do not depend on the nature of the alkoxy ligands. Additional fine structure due to *cc*/*ct* and *tt*/*tc* splittings is indicated on the spectra. The intensities for the *tt* and *tc* structures are comparable, but that for *cc* is stronger than for *ct* (which is necessarily equal to *tc*). This means that (-)-**3b** and **3b** have a somewhat blocky cis/trans distribution, as commonly found for metathesis polymerization of norbornene^{17,18} and its derivatives.⁹⁻¹⁶

DISCUSSION

One of the two important results that has been revealed in this study is that the cis content of polymers made from a norbornene correlates with the electrophilicity of the initiator. Such a correlation also has been found when 2,3-bis(trifluoromethyl)norbornadiene and 2,3-dicarbomethoxynorbornadiene are the monomers employed; all trans polymers are formed when OR = O-*t*-Bu² and all cis polymers when OR = OMe(CF₃)₂.⁶ This work establishes that the formation of high trans or high cis polymers is not restricted to norbornadienes, but is likely to be a more general feature of catalysts of this type. One potentially important feature of catalysts of this type is that the rate of isomerization of anti and syn alkylidene rotamers varies by many orders of magnitude, being relatively fast in **2a** (~ 1 s⁻¹) and slow in **2c**.⁷ It is now believed that high cis content polymers result from monomer addition to the syn alkylidene, and that high trans polymer is formed upon addition of monomer to the anti alkylidene (or to some other more

reactive intermediate during alkylidene rotamer isomerization), even though only syn rotamer can be observed readily in solution.¹⁹ The trans content of the polymers prepared here employing **2a** is approximately the same as the trans content of poly-2,3-bis(trifluoromethyl)norbornadiene prepared employing **2a**, but the cis content of the polymers prepared employing **2c** is only ~85% as opposed to essentially 100% in the case of poly-2,3-bis(trifluoromethyl)norbornadiene prepared employing **2c**.⁶ We could only speculate at this stage why **1** is not polymerized by **2c** to give 100% cis polymer.

A second important finding is that **3a** is atactic, while **3c** shows an isotactic bias. Poly-2,3-bis(trifluoromethyl)norbornadiene prepared employing **2c**⁶ shows a tactic bias of the same magnitude as that observed here for **3c**, but high trans poly-2,3-bis(trifluoromethyl)norbornadiene and poly-2,3-dicarbomethoxynorbornadiene prepared employing **2a** are highly tactic.² Recently we have proven that a variety of high cis polynorbornadienes and norbornenes, including **1**, that can be prepared with a chiral (racemic) catalyst, are isotactic, a result that is consistent with the conclusions reached here, and that all-trans poly-2,3-dicarboalkoxynorbornadienes in which a chiral group (e.g., menthyl) is present in the ester are syndiotactic.²⁰ Isotacticity is believed to be the result of addition of monomer to the same Mo=C face in the syn rotamer of each intermediate in the polymerization reaction. In the absence of a chiral ligand on the metal, tacticity is determined by chain-end control. Apparently the chain end control that gives rise to all trans syndiotactic polymers of 2,3-disubstituted norbornadienes is ineffectual in the case of polymerization of **1** by **2a**.

Tacticity (*m* and *r*) and XX/XN/NN-type structures are related in the polymerization of (+)-**1**, but are not necessarily related in the polymers derived from (±)-**1**. In the high-cis polymer **3c**, synthesized from (±)-**1**, no XN bias was found. This indicates that either enantiomer is equally likely to add to the growing polymer chain. However, some selectivity for tacticity was found for these polymers (~4:1 *m*:*r* dyads, evidenced by (-)-**3c**). This emphasizes that tacticity does not derive from XN-type selectivity, i.e., the chirality of the chain end is indifferent to the chirality of the incoming monomer. In other catalyst/monomer systems there is either little bias

in favor of *cis m* (e.g. $\text{WCl}_6/\text{SnBu}_4$ /*endo,endo*-5,6-dimethylnorbornene¹⁶) or a strong bias in favor of *cis r* (e.g. ReCl_5 /*endo,endo*-5,6-dimethylnorbornene¹⁶).

CONCLUSIONS

The ^{13}C NMR spectra of polymers of *endo,exo*-5,6-dimethylnorbornene made with well-characterized molybdenum alkylidene complexes have been assigned in detail. The *cis* content correlates with the electron-withdrawing ability of the alkoxy ligands, maximizing for the most electron-withdrawing hexafluoro-*t*-Butoxide ligand. The *cis* centered dyads have an isotactic bias $(\sigma_m)_c = 0.78$, but the *trans* centered dyads are atactic, $(\sigma_m)_t = 0.48$. There is no significant XN bias in either *cis* or *trans* centered dyads.

EXPERIMENTAL SECTION

General. All polymerizations were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl under nitrogen. Pyridine was distilled from calcium hydride. The THF used for polymerization reactions was vacuum transferred from sodium benzophenone ketyl and passed through activated alumina prior to use. (-)-Dimenthyl fumarate was prepared by treating fumaric acid and *l*-(-)-menthol (2 equiv) with a catalytic amount of *p*-toluenesulfonic acid in toluene, and heating the reaction mixture to reflux until no more water was evolved, as evidenced by separating the water in a Dean-Stark trap. After standard workup, the crude product (oil) was triturated with methanol to yield colorless crystalline material, which was used without further purification. $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})(\text{O-}i\text{-Bu})_2$, $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})[\text{OCMe}_2(\text{CF}_3)]_2$ and $\text{Mo}(\text{CH-}i\text{-Bu})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$ (Ar = 2,6-diisopropylphenyl) were synthesized as described in the literature.^{21,22}

NMR chemical shifts are listed in ppm downfield from TMS. Gel permeation chromatography (GPC) was carried out at room temperature using Shodex KF-802.5, 803, 804, 805, 800P columns, a Knauer differential refractometer, and either a Spectroflow 757 absorbance detector (254 nm) or a Viscotek Differential Refractometer/Viscometer H-500 on samples 0.1-

0.3 % w/v in THF that had been filtered through a Millex-SR 0.5 μ m filter in order to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd., 1206 to 1.03×10^6 MW). GPC data were analyzed using Unical 4.03 (Viscotek). A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine glass transition temperatures at a scanning rate of 20°C/min. Optical rotation was measured at 20°C with a Perkin-Elmer 24 polarimeter using a sodium lamp set at 589 nm (cell length = 1.0 dm).

Preparation of monomer. (+)-(2S,3S)-Dicarbomethoxynorborn-5-ene ((+)-5) was prepared by the asymmetric Diels-Alder reaction^{23,24} of cyclopentadiene (0.608 mole) and *l*-(-)-dimethyl fumarate (0.405 mole) in the presence of diethyl aluminum chloride (0.446 mole) in toluene (500 mL) at -78 °C under argon. Standard workup procedures, followed by recrystallization from methanol gave (+)-5 as colorless needles (yield 87%; $[\alpha]_D = +1.2^\circ$, $c = 10.0$ g/dL in CHCl_3): ^1H NMR (CDCl_3) δ 6.27 (dd, $J = 5.6, 3.2$, 1 H), 6.00 (dd, $J = 5.5, 2.8$, 1 H), 4.66 (ddd, $J = J' = 10.9, 4.3$, 1 H), 4.55 (ddd, $J = J' = 10.9, 4.3$, 1 H), 3.33 (dd, $J = J' = 4.2$, 1 H), 3.24 (broad, 1 H), 3.08 (broad, 1 H), 2.64 (dd, $J = 4.5, 1.7$, 1 H), 1.86-1.99 (m, 4 H), 1.57-1.68 (m, 6 H), 1.32-1.49 (m, 4 H), 0.76-1.06 (m, 6 H), 0.88 (d, $J = 6.5$, 6H), 0.87 (d, $J = 6.6$, 3 H), 0.86 (d, $J = 6.4$, 3 H), 0.73 (d, $J = 7.0$, 3 H), 0.71 (d, $J = 7.0$, 3 H).

(+)-Norborn-5-ene-(2S,3S)-dicarboxylic acid ((+)-6) was prepared by hydrolysis of 5 (0.351 mole) in hot methanol (1 L) and potassium hydroxide (1.8 mole) at reflux for 14 h under argon. The crude reaction mixture was concentrated to a solid, treated with water (650 mL) and extracted with ether (3 x 280 mL) to remove menthol. The aqueous layer was acidified to pH = 1 and extracted with ether (3 x 280 mL). The ether layers were combined, dried and concentrated, and the crude product was recrystallized from ethyl acetate/petroleum ether to give colorless crystals of (+)-6 (86%; $[\alpha]_D = +134.8^\circ$, $c = 5.0$ g/dL in MeOH): ^1H NMR (THF-d_8) δ 10.68 (broad, 2H), 6.22 (dd, $J = 4.2, 3.2$, 1 H), 6.06 (dd, $J = 5.6, 2.7$, 1 H), 3.30 (dd, $J = J' = 4.1$, 1 H), 3.17 (broad, 1 H), 3.06 (broad, 1 H), 2.58 (dd, $J = 4.1, 1.6$, 1 H), 1.60 (pseudo-doublet, $J = 8.3$, 1 H), 1.36 (dd, $J = 8.3, 1.8$, 1 H).

Reduction of (+)-6 (0.324 mole) with lithium aluminum hydride (1.05 mole) in ether (750

mL) at reflux under argon for 14 h yielded (–)-norborn-5-ene-(2S,3S)-dimethanol ((–)-7) as a colorless liquid after standard workup procedures. This was purified by vacuum distillation (103–104 °C / 0.15 mmHg; 88%; $[\alpha]_D = -21.5^\circ$, $c = 2.3$ g/dL in CHCl_3): ^1H NMR (CDCl_3) δ 6.21 (dd, $J = 5.67$, $J' = 3.15$, 1 H), 5.96 (dd, $J = 5.61$, $J' = 2.85$, 1 H), 3.76 (dd, $J = 9.77$, $J' = 5.51$, 1 H), 3.65 (dd, $J = 9.65$, $J' = 5.15$, 1 H), 3.40 (dd, $J = J' = 9.95$, 1 H), 3.02 (dd, $J = J' = 9.79$, 1 H), 2.80 (broad, 1 H), 2.57 (broad, 1 H), 2.43 (s, 1 H), 1.93 (m, 1 H), 1.42 (broad, 2 H), 1.30 (m, 1 H).

Compound (–)-7 (16.2 mmol) was treated with *p*-toluenesulfonyl chloride (65.0 mmol) in 50 mL of dry pyridine at room temperature for 14 h. The reaction was worked up by standard procedures and the product was recrystallized from ethyl acetate/hexane to give (+)-norborn-5-ene-(2S,3S)-dimethanol bis(4-methylbenzenesulfonate) ((+)-8) as colorless crystals (91%; $[\alpha]_D = +52.6^\circ$, $c = 5.0$ g/dL in CHCl_3): ^1H NMR (CDCl_3) δ 7.72–7.77 (m, 4 H), 7.32–7.35 (m, 4 H), 6.11 (dd, $J = 5.7$, 3.2, 1 H), 5.78 (dd, $J = 5.7$, 2.7, 1 H), 4.00 (dd, $J = 10.0$, 6.6, 1 H), 3.89 (dd, $J = J' = 9.2$, 1 H), 3.73 (dd, $J = 9.5$, 6.6, 1 H), 3.57 (dd, $J = J' = 9.6$, 1 H), 2.83 (broad, 1 H), 2.63 (broad, 1 H), 2.44 (s, 6 H), 1.86 (m, 1 H), 1.41 (dd, $J = 9.2$, 2.1, 1 H), 1.27 (dd, $J = 9.2$, 1.4, 1 H), 1.15 (m, 1 H).

(+)-(5R,6R)-Dimethylnorborn-2-ene ((+)-1) was prepared by the reduction of (+)-8 (19.8 mmol) with lithium aluminum hydride (198 mmol) in ether (300 mL) at reflux for one day under argon. The reaction mixture was cooled in an ice bath and then treated with 50 mL of saturated ammonium chloride solution. The inorganic solids were separated by filtration and washed with ether. The combined ethereal solutions were washed twice with sodium thiosulfate (10% w/w) solution followed by saturated sodium chloride solution. The ether solution was dried over CaCl_2 and ether was removed by distillation at atmospheric pressure. The product was distilled from sodium under argon at atmospheric pressure (128°C; 57%; $[\alpha]_D = +72.8^\circ$, $c = 2.8$ g/dL in CHCl_3). The optical purity of (+)-1 was found to be 96% (e.e.) according to GC analysis using a CHROMPACK CP-Cyclodextrin- β -2,3,6-M-19 column: ^1H NMR (CDCl_3) δ 6.20 (dd, $J = 5.7$, 3.1, 1 H), 5.96 (dd, $J = 5.8$, 2.7, 1 H), 2.59 (broad, 1 H), 2.31 (broad, 1 H), 1.46–1.51 (m, 2 H),

1.35-1.39 (m, 1 H), 1.06 (d, $J = 6.8$, 3 H), 0.85-0.88 (m, 1 H), 0.80 (d, $J = 6.9$, 1 H).

Polymerization of 1. Polymerizations of 100 equiv of (+)-**1** or (±)-**1** using **2a**, **2b**, or **2c** were conducted in THF at room temperature. The following is a typical example. A solution of (+)-*endo,exo*-5,6-dimethylnorborn-2-ene (**1**) (300 mg, 2.45 mmol) in 6.00 mL of THF was added in one portion to a rapidly stirred solution of Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)₂ (**2a**) (12 mg, 0.0245 mmol) in 6.00 mL of THF at room temperature and the mixture was stirred for 20 min. The living polymer was quenched by adding benzaldehyde (15 μ L). After 30 min, the reaction mixture was added dropwise to 150 mL of methanol. The colorless precipitate was isolated by centrifugation or filtration, washed with methanol, and dried under vacuum overnight. In all cases, yields were greater than 90%. GPC analyses, optical rotation and glass transition temperatures are presented in Table I. Samples for ¹³C NMR spectra were further purified by a second precipitation from THF into methanol. All optical rotations were measured at a concentration of 2.8 g/dL in CHCl₃ at 20°C.

¹³C NMR spectra. ¹³C{¹H} spectra on polymer samples (8-9 w/v% in CDCl₃) were obtained at 125.7 MHz on a Varian VXR-500 instrument at 25 °C with spectral widths of 25000 Hz and an acquisition time of 1.30 s. All chemical shifts were determined relative to TMS. The DEPT ¹³C{¹H} NMR spectra were obtained at 62.9 MHz on a Bruker AC-250 instrument with spectral widths of 20000 Hz, polarization transfer angle (Θ_y) of 135°, and acquisition time 0.41 s. The HETCOR 2D ¹³C-¹H spectra were obtained at 75.4 MHz (¹³C) using a Varian Unity 300 instrument with spectral widths of 11270 Hz, 2D spectral widths of 2018 Hz, and acquisition time of 0.09 s.

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Table I. Properties of polymers made from (+)-**1** and (±)-**1** using initiators **2a**, **2b**, or **2c**.^a

Monomer ^b	Initiator	Polymer	Yield (%)	σ_c^c	$10^{-4}M_n^d$	$10^{-4}M_n^e$	M_w/M_n	$[\alpha]_D^h$ (deg)	T_g (°C)
(+)- 1	2a	(-)- 3a	94	0.05	2.1	1.2 ^f	1.03	-23.8	55
(±)- 1	2a	3a	91	0.05	1.7	1.4	1.03		55
(+)- 1	2b	(-)- 3b	96	0.58	2.7	1.6	1.15	-31.7	75
(±)- 1	2b	3b	93	0.44	1.5	1.5	1.13		71
(+)- 1	2c	(-)- 3c	97	0.85	3.8	2.4 ^g	1.20	-53.6	85
(±)- 1	2c	3c	95	0.85	0.9	1.2	1.19		79

^a [1]/[2] = 100, except where indicated; ^{f,g} solvent = THF. Polymer was cleaved from the metal with benzaldehyde.

^b (+)-**1**: $[\alpha]_D = 72.8^\circ$ ($c = 2.8$ g/dL in CHCl_3 at 20°C; optical purity (e.e.) 96%).

^c Fraction of *cis* double bonds, as determined from the C_1 or C_6 fine structure in ^{13}C NMR spectra. Infrared bands at 970 cm^{-1} (*trans*) and 745 cm^{-1} (*cis*) provide qualitative confirmation for the *cis* and *trans* assignments.

^d Measured by absorbance detector (254 nm) relative to polystyrene standards. For 100% conversion of monomer, complete consumption of initiator, and allowance for $\text{Me}_3\text{CCH=}$ and $=\text{CHPh}$ end groups, calculated M_n values would be 1.2×10^4 .

^e Measured by on-line viscometry; calculated $M_n = 1.2 \times 10^4$.

^f [1]/[2] = 115; M_n (calcd) = 1.4×10^4 .

^g [1]/[2] = 133; M_n (calcd) = 1.6×10^4 .

^h Concentration = 2.8 g dL^{-1} in CHCl_3 at 20°C.

Table II. Predicted (from shifts in 4) and observed ^{13}C chemical shifts^a in the spectra of 3a and 3c.

Carbon in 4					Subst. Param.	Carbon in 3					
δ						Pred.		Obs(avg)	Obs		
Trans	C ₂	HH	133.26	0.23	C ₂	XX	133.49 (0.21) ^b	133.75 (0.18) ^b	{	133.81 ^c	<i>r</i>
										133.68	<i>m</i>
	C ₂	HT	131.45	1.83	C ₂	XN	133.28 (1.01)	133.56 (1.10)	{	133.66	<i>r</i>
										133.45 ^c	<i>m</i>
	C ₃	TH	135.46	-2.89	C ₃	NX	132.27 (0.27)	132.46 (0.20)	{	132.57	<i>r</i>
										132.34	<i>m</i>
	C ₃	TT	133.43	-1.43	C ₃	NN	132.00	132.26	{	132.34	<i>r</i>
										132.16	<i>m</i>
Cis	C ₂	HH	133.82	0.43	C ₂	XX	134.25 (1.17)	134.22 (0.98)			
	C ₂	HT	131.92	1.16	C ₂	XN	133.08 (0.39)	133.24 (0.81)	{	133.28 ^d	
										133.19 ^d	
		C ₃	TH	136.15	-3.46	C ₃	NX	132.69 (1.01)	132.43 (0.82)		
	C ₃	TT	134.42	-2.74	C ₃	NN	131.68	131.61			

^a Listed in order of decreasing chemical shift.

^b Bracketed values are differences between successive shifts.

^c Split further into doublet, see Figure 1(a), attributed to *rr/rm* triads for C₂ XX and *mm/mr* triads for C₂ XN.

^d The source of this splitting is not known.

Table III. Line positions and assignments for olefinic carbon atoms (C_2 , C_3) in polymers (-)-**3a** ($\sigma_c = 0.05$), (-)-**3b** ($\sigma_c = 0.58$), and (-)-**3c** ($\sigma_c = 0.85$).

Chemical Shift (ppm)			Assignment ^a								
(-)-3a	(-)-3b	(-)-3c	trans				cis				
	134.25 134.14 134.0 ^c	134.24 134.13 134.03	}				C ₂	cc/ct	XX	r	
133.83 ^b 133.78 ^b	133.82	133.81	}		C ₂	tt	XX	rr/rm			
133.68					C ₂	tc	XX	rr			
133.63	133.62	133.63			C ₂	tc	XX	rm			
133.45 ^b 133.39 ^b	133.37		}		C ₂	tt	XN	mr/mm			
133.30					C ₂	tc	XN	mr			
133.26	133.29	133.28			C ₂	tc	XN	mm			
	133.19 ^b 133.12	133.16 ^b (sh)	}				C ₂	cc/ct	XN	m	
132.57					C ₃	tc	(?)				
132.49	132.52	132.5 ^c					C ₃	ct	NX	m	
132.35 ^b	132.42 ^b	132.43 ^b	C ₃	tt	{	NX NN	m r	C ₃	cc	NX	m
132.17					C ₃	tc	(?)				
131.71 131.60	131.67 131.64	131.71 131.6 ^c	}				C ₃	cc/ct	NN	r	

^a*cc/ct* implies that both *cc* and *ct* resonances are present but individual assignments are uncertain; likewise for *rr/rm* and *mr/mm*.

^b Main peaks.

^c Shoulder.

Table IV. Assignment and line positions for olefinic carbon atoms in polymers **3a** ($\sigma_c = 0.05$) and **3c** ($\sigma_c = 0.85$) for those resonances not listed in Table III.

Chemical shift (ppm)		Assignment			
3a	3c	<i>trans</i>		<i>cis</i>	
	134.22			C ₂	cc/ct XX <i>m</i> ^a
133.68 ^b	{	C ₂	<i>tt</i>	XX	<i>m</i>
133.66 ^b		C ₂	<i>tt</i>	XN	<i>r</i>
	133.28	{		C ₂	cc/ct XN <i>r</i> ^a
	133.19				
132.57		C ₃	<i>tt</i>	NX	<i>r</i>
132.14		C ₃	<i>tt</i>	NN	<i>m</i>
	132.43			C ₃	cc/ct NX <i>r</i> ^a
	131.61			C ₃	cc/ct NN <i>m</i> ^a

^a *m/r* unresolved.

^b Overlap with C₂ *tc* XX *r* peaks (Table III) should be noted.

Table V. Predicted and observed line positions and assignments for the ring and methyl carbons in (-)-3a and 3a (Figures 2(a) and 2(b)). (Only *rr* peaks are listed.)

δ (ppm) for 4 ^a	Substn. param. ^b (ppm)	Predicted δ (ppm) 3	Carbon		Observed δ (ppm) (-)-3a	Provisional assignment ^c for (+)-3a	δ (ppm) 3a
52.2	-1.1	51.1	C ₁	{	51.16	NN- <u>XX</u> <i>rr</i>	51.22
							51.17
							51.15
					51.09	XN- <u>XX</u> <i>mr</i>	51.13
				51.07	NN- <u>XX</u> <i>rm</i>	51.11	
				50.99	XN- <u>XX</u> <i>mm</i>	51.02	
39.7	9.4	49.1	C ₆	{	47.50	XN <i>m</i>	47.51
						XN <i>r</i>	47.48
						XX <i>m</i>	47.39
					47.33	XX <i>r</i>	47.36
						45.15	
40.6	2.9	43.5	C ₄	{	45.06	NX- <u>NX</u> <i>mm</i>	45.08
					45.04	XX- <u>NX</u> <i>rm</i>	45.05
					44.94	NX- <u>NN</u> <i>mr</i>	44.97
					44.89	XX- <u>NN</u> <i>rr</i>	44.92
41.0	4.9	45.9	C ₅	{			44.86 ^d
							44.82 ^d
					44.71	NX <i>m</i>	44.75
					44.68	NN <i>r</i>	44.71
41.8	-2.2	39.6	C ₇	{			39.49
					39.39	XN-XN <i>mm</i>	39.39
					39.33	XN-XX <i>mr</i>	39.31
					39.28 ^e	NN-XN <i>rm</i>	
					NN-XX <i>rr</i>		
			C ₉ (X)	{	17.20	XN- <u>XX</u> <i>mm</i>	17.17
					17.09	NN- <u>XX</u> <i>rm</i>	17.08
					17.01	XN- <u>XX</u> <i>mr</i>	17.03
					16.91	NN- <u>XX</u> <i>rr</i>	16.92
			C ₈ (N)	{	15.77	NN <i>r</i>	15.79
					15.74	NX <i>m</i>	15.74

^a Ref. 9. Average values in the cases where there is fine structure.

^b On the basis of line positions for polymers of norbornene and *endo*-5-methylnorbornene.

^c Based on the assumption that $(\sigma_m)_t < 0.5$. The unassigned lines in the spectrum of 3a arise from the presence of additional structures, not possible in (-)-3a, e.g. for C₁ the NN-XX sequences may be *mm*, *mr*, *rm* as well as *rr*. Underlining in the Table denotes the unit within which the relevant carbon is contained.

^d Assigned mainly to C₅ NN*m* and NX*r*, but may contain a contribution from C₄.

^e Double intensity peak arising from two of the possible four structures listed.

Table VI. Predicted and observed line positions and assignments for the ring and methyl carbons in (-)-**3c** and **3c** (Figures 2e and 2f). (Only *cc* peaks are listed.)

δ (ppm) for 4a	Substn. param. ^b (ppm)	Predicted δ for 3 (ppm)	Carbon	δ (ppm) (-)- 3c	Assignment (-)- 3c	δ (ppm) 3c
40.7	9.2	49.9	C ₆	48.24	{ XN <i>m</i> XX <i>r</i>	49.28
47.5	-1.2	46.3	C ₁	{ 46.17 46.09 45.71	{ XX <i>r</i> XN <i>m</i>	sh ^d 46.08 45.72
42.0	4.4	46.4	C ₅	{ 44.88 44.71	{ NN <i>r</i> NX <i>m</i>	44.87 44.71
43.0	-1.8	41.2	C ₇	sh 40.94 40.66	{ NN-XX <i>rr</i> XN-XN <i>mm</i> NN-XN <i>rm</i> ^e XN-XX <i>mr</i> ^e	41.14 40.91 40.66
36.0	2.1	38.1	C ₄	{ 39.38 39.10	{ NX <i>m</i> NN <i>r</i>	39.39 39.12 39.04 ^f
			C ₉ (X)	17.45	{ XN <i>m</i> XX <i>r</i>	17.48
			C ₈ (N)	15.64	{ NN <i>r</i> NX <i>m</i>	15.64

^aSee footnote a in Table V.

^bSee footnote b in Table V.

^cBased on the fact that $(\sigma_m)_c = 0.78$ (from C₂, C₃ intensities).

^dShoulder.

^e*mr* and *rm* assignments may be reversed.

^fAssigned to NN *m*. No other resonances for **3c** show *m/r* splitting.

FIGURE CAPTIONS

Figure 1. 125 MHz $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of the olefinic carbon atoms in polymers **3a** - **3c**: (a) (-)-**3a**, $\sigma_c = 0.05$; (b) **3a**, $\sigma_c = 0.05$; (c) (-)-**3b**, $\sigma_c = 0.58$; (d) **3b**, $\sigma_c = 0.44$; (e) (-)-**3c**, $\sigma_c = 0.85$; (f) **3c**, $\sigma_c = 0.85$. In Figure 1(d) only the main lines from Figures 1(b) and (f) are marked. The other lines arise from *cc/ct* and *tt/tc* splittings.

Figure 2. 125 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the ring and methyl carbon atoms in polymers **3a**-**c**: (a) (-)-**3a**, $\sigma_c = 0.05$; (b) **3a**, $\sigma_c = 0.05$; (c) (-)-**3b**, $\sigma_c = 0.58$; (d) **3b**, $\sigma_c = 0.44$; (e) (-)-**3c**, $\sigma_c = 0.85$; (f) **3c**, $\sigma_c = 0.85$.

